Neutral Products Desorption from DNA Thin Films Induced by Low-Energy Electrons (0.5-20 eV)

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Low-energy electrons (LEEs) are produced in great amount in the biological medium, when submitted to high-energy radiations. They have the ability to induce strand breaks in the DNA duplex, as proven by electrophoresis analysis of irradiated dry deposits [1]. LEE interactions with target molecules induce the formation of different species such as anions, cations, radicals and neutrals. The desorption of anionic species from oligonucleotides and DNA under LEEs irradiation has been intensively explored [2,3]. The involved mechanisms and sites were successfully identified, including the resonant formation of transient negative ions (TNI) below 15 eV. However, the desorption of neutral products was less explored [4], due to their difficult detection. Exploring this aspect will provide additional information and complete the picture of the dissociating pathways followed by TNIs.

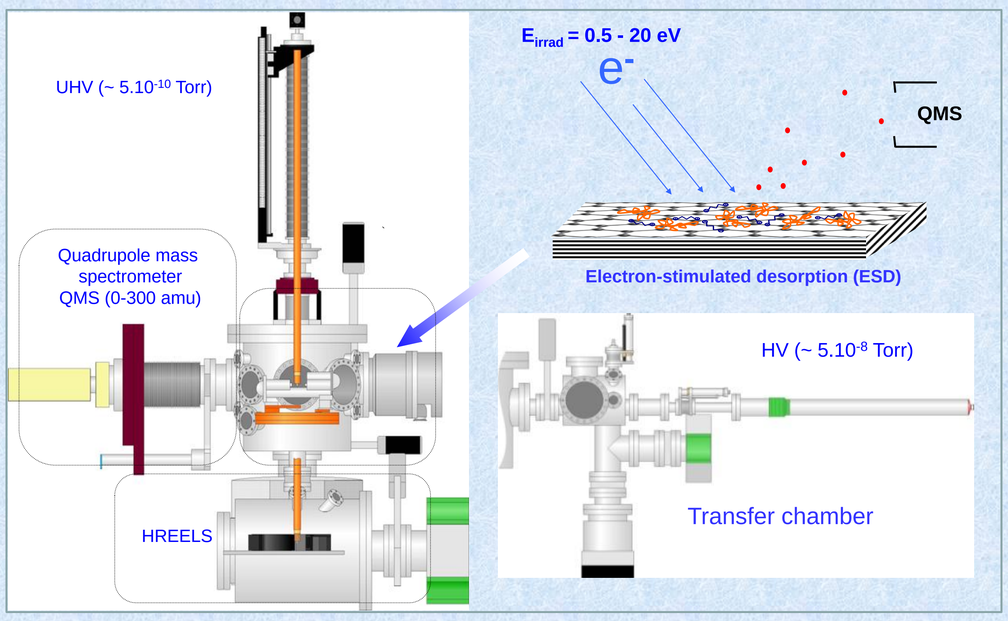

Fig. (2) *Electron Stimulated Desorption (ESD) analysis setup. Samples can be transferred into the irradiation chamber for desorption experiments without backing. Irradiations are carried out using a home made electron gun (ϕ_{target} ~1 cm). The current is measured directly on the target fig.(5).*

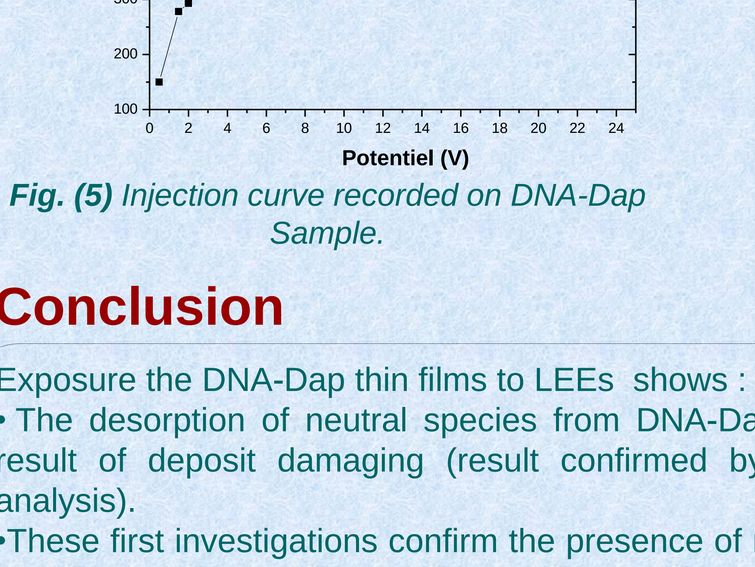

Fig. (4) *Raw data from QMS. The electron gun is switched on/off every 5 minutes and the energy is increased step by step.*

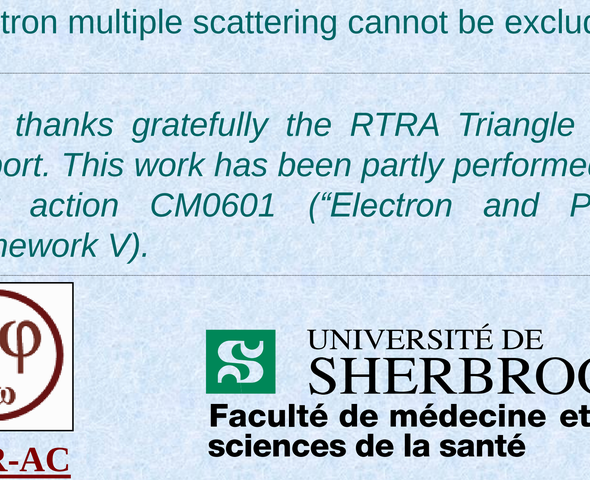

Fig. (5) *Injection curve recorded on DNA-Dap Sample.*

Materials and methods

We used electron ionization quadrupole mass spectrometry (QMS at 70 eV) to analyze neutral products, desorbing from DNA-diamine thin films (10 nm) under (0.5-20 eV) electron irradiation. We quantified DNA damages after irradiation by electrophoresis analysis.

Target preparation [5]
1- Highly Oriented Pyrolitic Graphite (HOPG): an atomically smooth and hydrophobic surface.
2- Deposition of a DNA plasmid (~3 kbp) by complexation with Diaminopropane dichlorohydrate (Dap) without buffer.

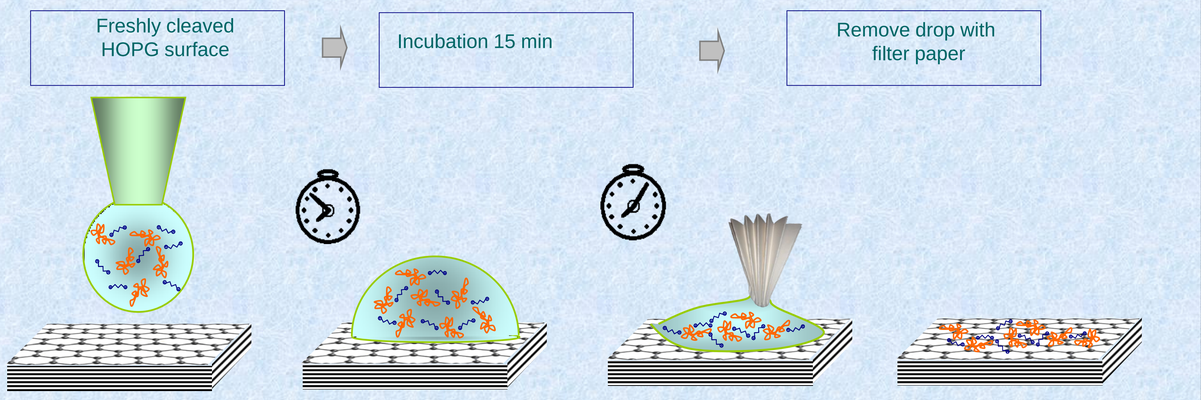

Fig. (1) *Protocol for thin DNA-diamine film deposition*

Target caracterisation by AFM and electrophoresis gel

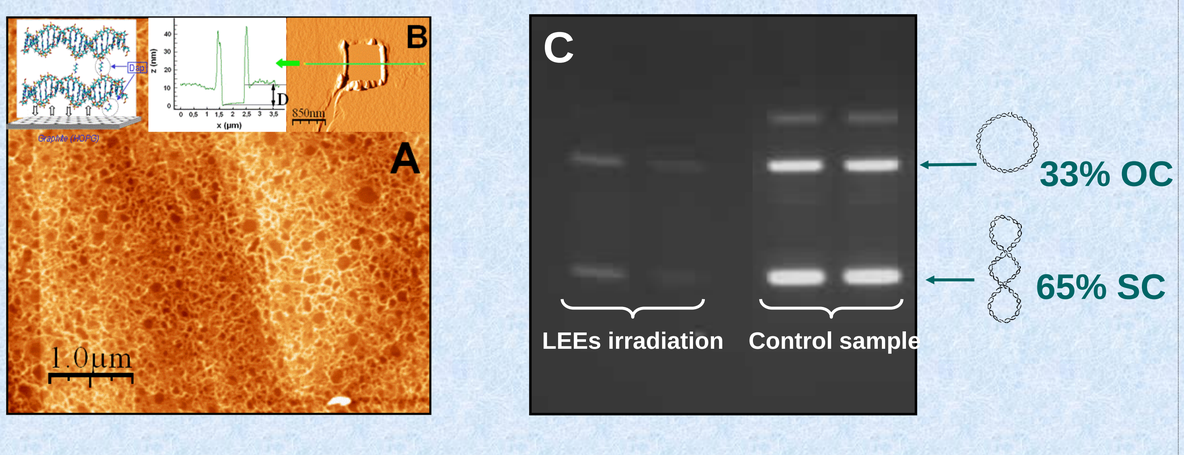

Fig. (3): *A) AFM image using the tapping mode obtained from DNA-Dap complex deposited on HOPG [5]. AFM image shows a very thin and homogeneous film. B) illustration of the thickness measurement by « AFM scratching ». C) gel electrophoresis analyses of the re-dissolved deposit before and after electrons irradiation.*

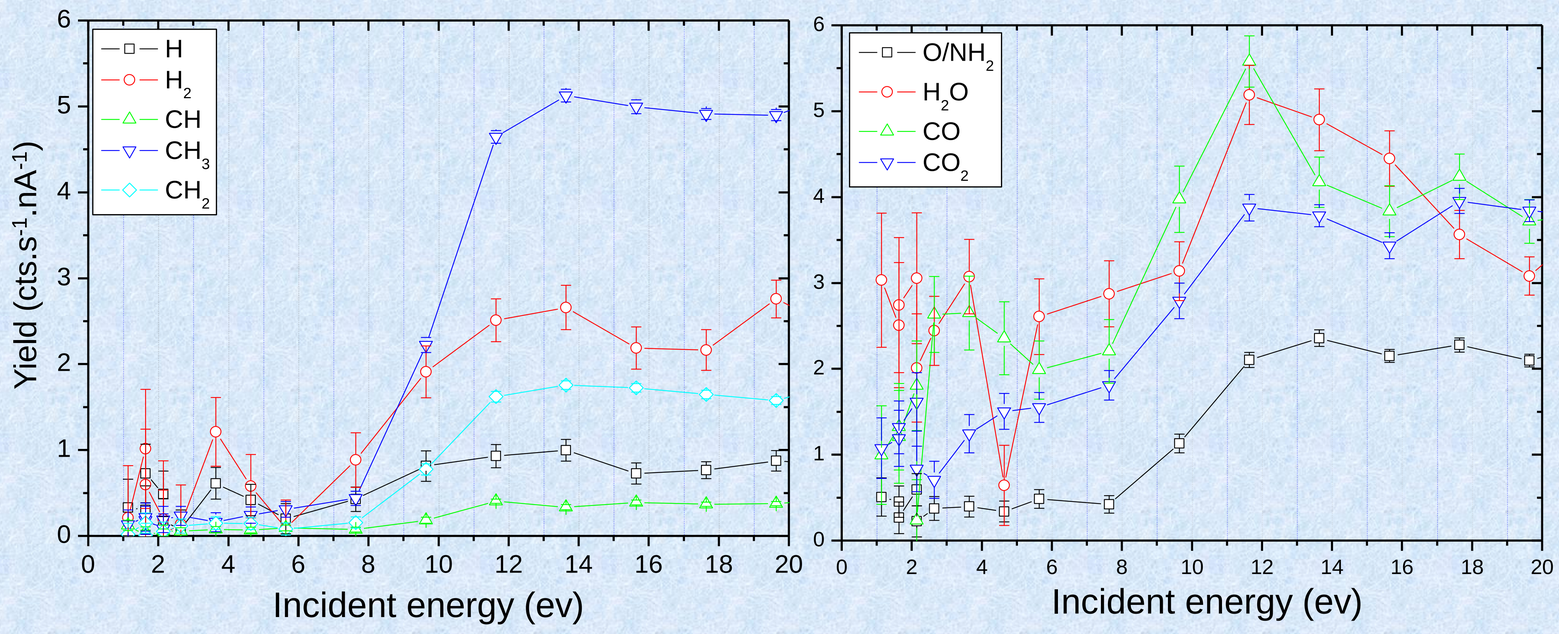

Fig. (6) *Yields of neutral species desorbing from a DNA-Dap thin film (10 nm thickness) versus the irradiation electron energy. Some species exhibit resonant structures at very low energy (around 1.5 and 3.5 eV). We attribute these resonant features to the TNIs observed by electrophoresis at 0.8 0.3 and 2.2 eV [6] . Above 6 eV, most of the desorption yields increase with a broad resonant structure around 13 eV.*

Conclusion

Exposure the DNA-Dap thin films to LEEs shows :
• The desorption of neutral species from DNA-Dap complex to be the result of deposit damaging (result confirmed by electrophoresis gel analysis).
•These first investigations confirm the presence of resonant structures at low energy (below 6 eV) associated to the dissociative decay of TNIs. [1,6]
•Resonant (broad structure around 13 eV) and non resonant dissociative channels contribute to the neutral yields above 6 eV. The contribution of electron multiple scattering cannot be excluded.

Prospects

Some points remain to be improved such as:
• measurement of the incident flux (nA.cm^{-2})
• determination of the Dap contribution to the desorption yields and evaluation of the impact of the DNA close-environment on its sensitivity to LEEs (using DNA lyophilised deposit)
• identification of responsible sites for the desorption of neutral species.

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References

*[1] B. Boudaiffa et al., Science, 287, **2000**, 1658.; [2] S. Ptasinska et al J. Chem. Phys. 123(12) **2005,** 124302-8.*
*[3] L. Sanche, Eur. Phys. J. D, 35, **2005**,367-390.*
*[4] H.Abdoul-Carime et al. Rad. Res. 156, **2001**, 151–157.; Y. Chen et al, Int. J. Mass Spectro 277, **2008**, 314–320.*
*[5] O. Boulanouar et al. Accepted in J. Phys. Chem. C. 10.1021/jp207083r **2011**.*
*[6] Martin F. et al.,Phys. Rev. Lett. 93 (6), **2004**, 68101-4 .*